CALCULATIONS OF THE NUCLEAR QUADRUPOLE COUPLING CONSTANT FOR I_2

D. V. G. L. NARASIMHA RAO

PHYSICS DEPARTMENT, ANDHRA UNIVERSITY, WALTAIR

(*Received, February* 16, 1959)

ABSTRACT. Certain theoretical studies on the quadrupole coupling constant of I^{127} in I_2 molecule are made following the general principles of Townes and Dailey (1949). The I–I bond is assumed to be one of a covalent type. Effects of *sp*-hybridization are considered and the results indicate the possibility of considerable amount of hybridization of the bonding orbitals.

INTRODUCTION

Though a number of values of the quadrupole coupling constant eqQ were accumulated for several nuclei in various molecules both from pure quadrupole spectra and also from a study of the hyperfine structure of rotational spectra in the microwave region, theoretical calculations were made only for a few molecules. The fundamental principles underlying the interpretation of the observed data and also some approximate methods for their theoretical evaluation were outlined by Townes and Dailey (1949). It is known that a knowledge of eqQ gives useful information about the pattern of chemical bonding in the molecules. In the description of Townes and Dailey, the charges which influence $q\left(= \frac{\partial^2 v}{\partial z^2}\right)$, the field gradient) at a particular nucleus in the molecule are divided as due to (i) the inner core electrons, (ii) valence electrons and (iii) the electrons and nuclei external to the atom under consideration. The contribution to q of the valence electrons which have a high probability of being found near the nucleus is shown to be larger by an order of magnitude than the contribution due to other charges.

A theoretical study of the ionic character and hybridization in HCl was made by Schatz (1954) in terms of an *spd*-hybrid valence bond function including an ionic term. The quadrupole coupling constant was found to depend principally on the ionic character and could not distinguish among the various possible sets of hybridization. Similar conclusions were drawn for Cl_2 (Schatz-1954a) and also for CH_3Cl by the same author (1954b).

Calculations of the quadrupole coupling constant of I^{127} in I_2 molecule are made by the present author using a simple model and the results of the investigation are given below.

CALCULATIONS AND RESULTS

Since the two atoms forming the bond are the same, the bond may be assumed to be one of a covalent type. The bonding wave function of I_2 may hence be written on the atomic orbital approximation as

$$\chi_b = A[\psi I_1(1)\psi I_2(2) + \psi I_1(2)\psi I_2(1)]$$

where ψI_1, ψI_2 are the bonding wave functions of I_1, I_2 atoms respectively and A is a normalisation factor given as $A = 1/(2+2S^2)^{\frac{1}{2}}$ with S as the overlap integral of ψI_1 and ψI_2. Assuming only sp-hybridization, the ψI's are

$$\psi I_1 = a\,\psi I\ (5s) + b\,\psi I(5p_z)$$
$$\psi I_2 = a\psi I(5s) + b\psi I(5p_z)$$

the z-axis being taken to represent the internuclear axis. The normalization condition gives $a^2+b^2 = 1$. The wave function of the non-bonding s-electrons (the lone-pair) consequently becomes

$$\chi I_{nb} = (1-a^2)^{\frac{1}{2}}\psi I(5s)+a\,\psi I(5p_z).$$

The iodine quadrupole coupling constant in I_2 may be regarded as due to (*i*) the electron pair forming the bond, (*ii*) the pairs of electrons $5p_x$ and $5p_y$ assumed to remain in non-bonding orbitals and (*iii*) the lone-pair electrons which make a non-zero contribution to eqQ since ψI is a sp-hybrid function.

The contribution of the first factor is given as

$$2eQ \int \chi_b{}^2 \frac{(3\cos^2\phi - 1)}{r^3}\,\partial\tau$$

where Q is the nuclear quadrupole moment of I^{127}. $\chi_b{}^2$ is the square of the bonding wave function integrated over electron (2) and ϕ, r are the polar co-ordinates of electron (1). Similarly for the contribution of the lonepair we may write

$$2eQ \int \chi_{nb}{}^2 \frac{(3\cos^2\phi - 1)}{r^3}\,\partial\tau$$

To evaluate the second factor we make use of the result that

$$2q_{px} + 2q_{py} + 2q_{pz} = 0$$

(*i.e.*, when the p shell is completely filled, its contibution to q is zero) and hence its contribution is $-2eQq_{pz}$. Making use of the symmetry and orthogonal properties of the wave functions it can easily be seen that the quadrupole coupling constant of I^{127} in the I_2 molecule is given as

$$eQq = \left[\ b^2/(1+S^2) - 2b^2\ \right] eQ \int \psi^2_{5pz} \frac{(3\cos^2\phi - 1)}{r^3}\,\partial\tau$$

$$= (eQq)_{atomic}[b^2/(1 + S^2) - 2b^2].$$

The results of the calculations are shown in the table below. Slater type wave functions are used and the required overlap integrals are read from Mulliken's (1949) Master tables. The value of the quadrupole coupling constant of a free I^{127} atom (eQq_{p_z}) is assumed as 2500 Mc/s. as given by Townes and Dailey (*i.e.*

$$eQ \int \psi^2_{5p_z} \frac{(3\cos^2\phi - 1)}{r^3} \partial\tau = 2500 \text{Mc/s})$$

TABLE 1

Percentage *s*-character	$\frac{eQq}{\text{Mc/s.}}$
0	2725
5	2689
10	2578
15	2456
20	2332
25	2187
26	2161
27	2130
30	2046

The observed value of the quadrupole coupling constant of I^{127} in I_2 is reported to be 2153 Mc/s. (Dehmelt, 1950) from a study of the pure quadrupole spectrum. It may be seen from the table that about 26 percent *s*-hybridization of the bonding orbital is necessary to account for this value. No investigation could be made on the microwave spectrum of I_2 molecule since it is homonuclear and hence the gas value of eQq is not available. The low value of eQq in the solid state as compared to the value assumed for the free atom has been attributed by Townes and Dailey (1952) to the formation of weak intermolecular bonds. The actual *s*-hybridization may be much less than the 26 percent assigned from data on the solid state. But it may be mentioned that even though it is assumed that the molecular eQq is near about the free atomic value of 2500Mc/s., the bonding orbitals must involve about 10 per cent *s*-character. This happens because of the overlap S between the two bond wave functions. Similar conclusions were reached by Schatz (1954a) for Cl_2.

The conclusions remain essentially the same also when the calculations are carried out based on the picture of Gordy (1951) with the value of 2153 Mc/s for the atomic eQq of I^{127} as assumed by him.

ACKNOWLEDGMENTS

The author is deeply indebted to Prof. K. R. Rao for his kind and invaluable guidance throughout the progress of work. His grateful thanks are aso due to the Council of Scientific and Industrial Research for financial assistance.

REFERENCES

Dehmelt, H. G., 1950, *Die Naturwissenschaften*, **37**, 398.
Gordy, W., 1951, *J. Chem. Phys.*, **19**, 792.
Schatz, Paul, N., 1954, *J. Chem. Phys.*, **22**, 695.
Schatz, Paul, N., 1954a, *J. Chem. Phys.*, **22**, 755.
Schatz, Paul, N., 1954b, *J. Chem. Phys.*, **22**, 1974.
Townes C. H. and Dailey, B. P., 1949, *J. Chem. Phys.* **17**, 782.
Townes C. H. and Dailey, B. P., 1952, *J. Chem. Phys.* **20**, 35.